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INFO-0345

DETERMINATION OF THE FEASIBILITY OF DIRECTLY DATING QUARTZ BY ELECTRON SPIN RESONANCE

by

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A research report prepared for the
Atomic Energy Control Board
Ottawa, Canada

Project No. 3.101.1

October 1988

Canada

Research report

90-05697/1

DETERMINATION OF THE FEASIBILITY OF DIRECTLY DATING QUARTZ BY ELECTRON SPIN RESONANCE

ABSTRACT

Electron spin resonance (ESR) analyses have been made of natural quartz samples ranging in age from 100 ka to 1.4 Ga. Signal intensities of two ESR centres that can be associated with Schottky-Frenkel (SF) defects are significantly correlated with age. These defects are thought to accumulate naturally as a result of elastic collisions in the quartz lattice initiated by the recoil of alpha-emitting nuclides present in the impurities. Preliminary indications are that recoil-induced SF defects can be significantly more abundant than original SF defects in samples older than several million years. These considerations provide the theoretical basis for a long-ranging quartz geochronometer.

RÉSUMÉ

Des échantillons de quartz naturel dont l'âge variait entre 100 000 ans et 1,4 milliard d'années ont été soumis à des analyses de résonance paramagnétique électronique. On a pu montrer que les intensités de signal de deux centres de résonance paramagnétique électronique qui peuvent être associées aux défectuosités de Schottky-Frenkel étaient étroitement reliées à l'âge. On croit que ces défectuosités s'accumulent naturellement par suite des collisions élastiques dans le réseau du quartz provoquées par la démagnétisation des nucléides qui sont contenus dans les impuretés et qui émettent des rayons alpha. Selon les premières indications, on est porté à croire que les défectuosités de Schottky-Frenkel produites par la démagnétisation peuvent être beaucoup plus abondantes que les défectuosités originelles de Schottky-Frenkel des échantillons d'au moins plusieurs millions d'années. Ces arguments servent de base théorique pour mettre au point un géochronomètre à quartz de longue portée.

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I INTRODUCTION

The ability to directly date faults and fractures is important in trying to establish the stability or instability of an area being considered for the construction of engineered structures such as nuclear power plants, radioactive waste repositories and dams. However, in eastern North America the direct dating of fault movements and, consequently, an assessment of tectonic stability, is particularly difficult. There are several reasons for this. First of all the youngest exposed rocks are commonly Precambrian, or Paleozoic in age. (Younger materials, such as Mesozoic rocks and Pleistocene to Recent sediments are also present, though they are definitely subordinate in number to the older rocks.) Furthermore, good exposures showing cross sectional relationships between the older and much younger rocks are lacking and datable, fault- and fracture-filling materials are not particularly abundant. Thus, in general, all that can be said about fault movements is that they are younger than the rocks they cut.

Quartz is a common fault- and fracture-filling mineral, appearing both in a massive habit or as slender, acicular crystals. The latter condition obtains where the rate of quartz precipitation in a fracture or fault keeps pace with the rate of fracture opening, or fault movement. If these crystals could be dated, then the age of the fault, or at least the age of last movement along the fault in which these crystals lie, could be determined.

Whether quartz occurs as delicate needles, or as massive

material, its common occurrence in faults and fractures makes it a tempting target for geochronological studies. If amenable to direct dating, it could contribute substantially to overcoming the problems of assessing the tectonic stability of an area.

Most standard geochronological techniques rely on the predictable decay of radioactive elements and are, therefore, not applicable to quartz because of the negligible concentrations of radioactive materials contained within the quartz lattice. Nonetheless, dating of quartz by electron-spin resonance (ESR) has been attempted with some measure of success, though up to now it has been limited to dating quartz which is no older than about 2 ma.

The purpose of this investigation was to determine whether or not quartz of any age might be datable by the use of ESR. If successful, the technique might then be applied to quartz from fault zones.

II PHYSICAL CONSIDERATIONS

1. Electron Spin Resonance and ESR Spectroscopy

ESR spectroscopy permits the detection and characterization of paramagnetic species. Paramagnetism results when unpaired electrons exist within a substance. A paramagnetic center which is the result of one unpaired electron can exist in either of two energy states, when the center is placed within an applied magnetic field. The energy separation of the two states depends on the magnetic field strength. For an ensemble of these types of centers, transitions can be induced between the two states when an additional perturbation (radiation in the microwave region which corresponds to the energy separation of the two permitted states at a particular magnetic field strength) is applied to the sample. Because at room temperature there is a slightly greater population of centers in the lower enery state, there is a net absorption of the microwaves. This will result in a change in microwave intensity that can be measured by means of an ESR spectrometer. At lower temperatures, there will be a greater population of electrons in the lower energy state, a greater microwave absorption by the sample, and hence a larger ESR signal.

Because a phase contrast detection system is utilized by the ESR spectrometer to measure microwave absorption, the ESR signals generated are the first derivatives of the absorption curves (see for example Figure 2).

For a selected frequency of microwaves, different types of paramagnetic centers will have transitions occurring between the

two energy levels at different magnetic field strengths. It is possible to characterize the detailed nature of the environment of the electrons and to identify what type of center is responsible for a particular ESR spectrum. In addition to providing structural information about the paramagnetic center, ESR spectroscopy can be used to measure the number of such centers in a sample. A detailed account of ESR phenomena and spectroscopy is given by Wertz and Bolton (1986).

2. Point Defects in Quartz

Natural quartz contains both intrinsic and extrinsic point defects. Some of these are the structural precursors to ESR centers that have been used in ESR dating attempts. Extrinsic defects of interest are formed where a foreign atom such as Al or Ge substitutes for silicon in the tetrahedral site of the quartz lattice. Intrinsic point defects are Schottky defects which are lattice vacancies and Frenkel defects in which one of the constituent atoms ocuppies an interstitial lattice position.

3. Radiation Induced ESR Centers In Quartz

effect of radiation on the electronic structure of quartz

Natural quartz is subjected to ionizing radiation, originating primarily from radioactive K, U, Th and, uranogenic and thorogenic short-lived radionuclides. In rare cases, radionuclides such as ^{147}Sm might be important, and in rocks exposed for sufficient time at the Earth's surface, cosmic radiation can be significant. Alpha particles, beta electrons, and high energy photons (gamma) which are emitted during the the

decay of ^{40}K, ^{238}U (^{235}U is less than 1% of natural U), ^{232}Th and the U-Th daughters are the important sources of ionizing radiation. Ionization of the quartz lattice occurs as a result of the transfer of energy from the alphas, betas, or gammas to the electronic field of the lattice with which they interact. By such interactions alpha and beta particles are eventually slowed and stopped and the energy of the gamma photons are absorbed by the quartz. Because there is an inverse relationship between specific ionization (ionizing power) and range, the relative effectivness of a, b, and gamma radiation depends on scale.

As a result of the ionizing effect of radioactivity, some electrons can acquire sufficient energy to elevate them to the conduction band level, thereby leaving a hole in the valance band. Room temperature life times of such conductive-electron/hole pairs are extremely short as they tend to quickly recombine. In natural quartz some of the conductive electrons and holes can be trapped within the band gap at defects in the lattice, where the likelyhood of recombination is greatly reduced, and their lifetimes thus extended. By trapping electrons and holes, these defects become centers of electrons that are not spin-paired, i.e. they become ESR centers. The larger the dose of ionizing radiation, the greater the number of conductive electron/hole pairs produced, and thus the greater the chance that some will be trapped at lattice defects to form ESR centers. This is the concept on which ESR dating has been based.

In particular, the response of four types of point defects

to ionizing radiation and the ESR centers that develop there have been the foci of attempts to date quartz.

Al hole centers

The nature of Al hole centers was first described by Griffiths and others (1954 and 1955) and O'Brien (1955). When trivalent Al is substituted for Si^{+4} in the tetrahedral site in quartz, there is one electron associated with the tetrahedron that is in excess of what is necessary for the local stability of the lattice and the overall charge balance of the crystal. In natural quartz this charge imbalance is normally compensated by localization of a cation such as H^{+1}, Na^{+1}, or Li^{+1}. This aluminum center is a non-paramagnetic species of the type $[AlO_4/M^{+1}]^{o}$ (Weil,1984). When irradiated at temperatures above 200° K (the thermal threshold to drive difussion of the charge compensating cations along the large c-axis channels), the difussing cations no longer remain localized, and Al centers are predominantly of the type $[AlO_4]^{-1}$ (Halliburton, 1985). Such species are also non- paramagnetic, but because of the charge imbalance they can readily trap migrating holes in the valance band to produce a quasi-stable ESR center of the type $[AlO_4/hole]^{o}$. There are actually several different species of paramagnetic Al centers, and these have been discussed by Weil (1984).

Ge electron centers

As with the case of Al centers, there are several different species of Ge centers (Isoya and others,1978; Weil,1984). The

basic Ge center is $[GeO_4]^-$, and it is thought to form by trapping an electron. This particular center is unstable at room temperature. At room temperature, the most common species is of the type $[GeO_4/M^+]^o$, where the charge is compensated by a cation such as Li^{+1}. The decay of the ESR signal associated with the uncompensated Ge center has been monitored in gamma irradiated quartz from Li rich pegmatites (Rink and Odom, 1988; unpublished manuscript included here a Appendix A) and found to have a room temperature half-life of approximately 30 minutes. The growth of the compensated occured simultaneously, suggesting that the rate was controlled by the diffusion of Li and perhaps Na ions.

E' centers

An E' center in quartz has been characterized as an unpaired electron localized at an oxygen vacancy (Schottkey defect) (Yip and Fowler, 1974; Jani and others, 1983). The formation of an E'center probably involves the trapping of a migrating hole (releasing an electron) within a non-bonding orbital. The E' center signal has been observed to increase in samples subjected to ionizing radiation (because of increase production of holes) and with the displacing bombardment of fast neutrons (presumeably because of production of new Schottkey defects).

Peroxy Radical centers

Stapelbroek et al. (1979), Friebele et al.(1979), and Friebele and Griscom (1979) have characterized a Frenkel defect in fused silica that is a :Si:O:O:Si: linkage (an interstitial oxygen). They pointed out that upon irradiation or heating, the linkage readily sheds an electron (traps a hole) to produce a

dangling peroxy radical, :Si:O:O., and thus an ESR center.

The peroxy radical (PR) center appears to be the same ESR center that Weeks (1956) observed in synthetic quartz subjected to fast-neutron irradiation. McMorris (1970) observed the signal in a number of samples of natural quartz and noted that, while little affected by gamma radiation, the signal grew with fast-neutron bombardment. This implies that elastic collisions and displacments of atoms were required. McMorris concluded that the natural production of this signal in quartz must involve knock-ons and displacements by the recoiling nuclei of alpha-emitting impurities. He proposed that the abundances of these centers in a specimen is a function of its alpha activity and age.

III ESR DATING OF QUARTZ

1. A Review of Conventional Methods and Applications

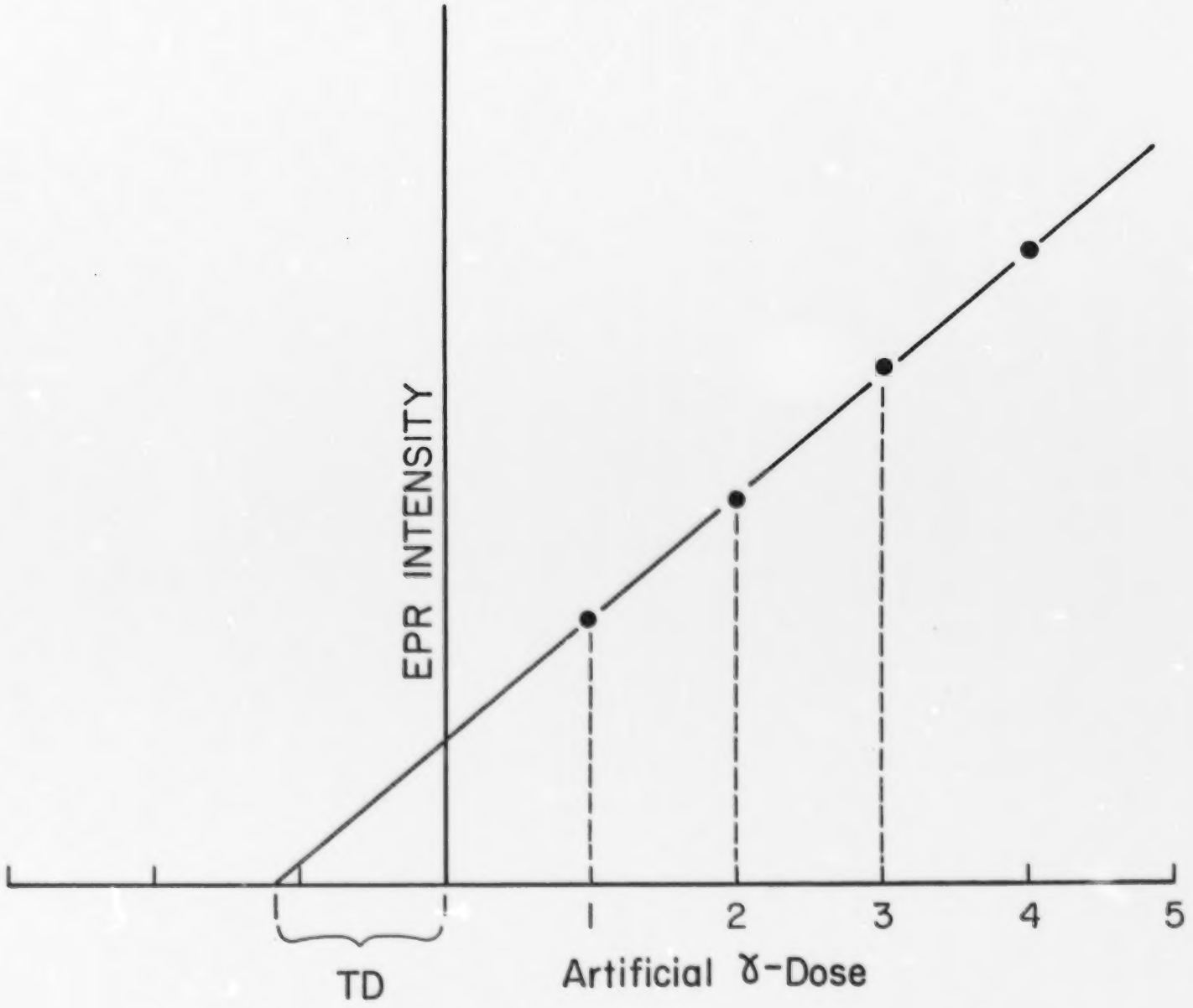
Zeller and others (1967), Zeller (1968), and Morency and others (1969) first proposed that the intensity of certain ESR signals in minerals could serve as a means of dating minerals. Like thermoluminescence, the ESR signal was observed to increase with artificial ionizing radiation up to the point of saturation where existing electron and hole traps are presumably filled. Figure 1 illustrates the method normally used. The sample is analyzed, and the signal intensity of the center (s) of interest is determined. The sample is then subjected to a known dose of artificial gamma radiation, and the ESR spectrum measured again. After a number of such additive doses and ESR intensity measurements, the data points on the plot in Figure 1 are back-extraplolated to zero ESR intensity, and the x intercept taken to be equivalent to the total dose TD that was required to produce the natural signal intensity.

In order to determine the ESR age of the sample, the natural dose rate must be determined. Two approaches have been used. One is to place a field dosimeter in the position of the sample and monitor the radiation level over a period of time. The other has been to determinine the U, Th, and K concentrations in the rock or material surrounding the sample and in the sample, and with certain assumptions (Hennig and Grun, 1983) calculate annual dose AD. The ESR age is then calculated as AGE = TD/AD.

Ikeya and others (1982) first applied this method to quartz. They utilized the rate at which an E′ center (described below) is

FIGURE 1.

The additive dose method of ESR dating: back-extrapolation of the increase in ESR signal intensity with artificial radiation dose yield the natural Total Dose of the sample.


EPR INTENSITY
1
2
3
4
5
TD
Artificial γ-Dose

increased by incremental gamma irradiation. Fukuchi and others (1986) reported on an attempt to date fault movement by the ESR age of quartz. In as much as in neither of these cases was the age of the quartz samples independently established, it is difficult to judge the success of the method. Shimokawa amd others (1984) and Imai and others (1985) successfully reproduced ages independently determined on volcanic ash. They utilized an Al center, Ge center, and a center they interpreted as an oxygen hole center. Shimokawa and others (1987) determined what they interpreted as both eruption ages and alteration age on volcanics. In these volcanics, it is somewhat disconcerting that different ESR centers from the same samples yield different ages. However authors inferred that the most stable center yielded an age close to the value determined by other techniques.

An excellent review of ESR dating is given by Hennig and Grun (1983).

2. Limitations and Problems of Method

Under the best of circumstances, conventional ESR dating is limited to quartz less than a few million years. There are two main reasons for this. One is that the concentration of original electron and hole trapping centers in quartz is limited, and once these approach saturation, growth in the ESR signal with artificial ionizing radiation is non linear. The background radiation in most quartz bearing rocks is sufficient to saturate the more stable traps in geologically short times. A second reason is that the depth of such traps are quite shallow (on the order of an electron volt), and hence their meanlives at ambient

geologic temperatures are relatively short.

A severe difficulty with the conventional approach to ESR dating of quartz is the determination of the annual dose the sample has received. The method used in the published studies cited has been to calculate the dose from the measured concentration of K, U, and Th in the host rocks of the quartz. One problem is evaluating the relative contribution of the natural alpha, beta, and gamma radiation in producing the observed ESR signals. There is an inverse relationship between the specific ionization and range in silicates of these types of radiation, so that while the range of alphas is limited to a few tens of microns, their ionizing strengths are an order of magnitude greater than that of betas (range a few mm). Beta electrons have a greater specific ionization than the highly penetrating gamma radiation. The radioactive elements in rocks are concentrated in specific minerals (of which quartz is not one) and sometimes along grain boundaries and fractures. Rocks are mineralogically and chemically rarely homogeneous on the scale of mm (glassy volcanics might be an exception) and never on the scale of microns.

Another problem is due to the extreme mobility of U under oxidizing conditions near the surface of the Earth, where it forms the stable and highly soluble uranyl ion. The leaching of U from rocks in zones of oxidation and its deposition in reducing environments is well documented (Rogers and Adams, 1969). In non-glassy igneous rocks, U is often concentrated along grain boundaries where it is easily removed. Recent removal of U from

cubic kilometers of granite has been documented (Rosholt and Bartel,1969). The leaching, transportation and deposition of U in sedimentary rocks is a well understood process that even produces economic deosits. The common ocurrence of unsupported uranogenic lead in igneous, sedimentary, and metamorphic rocks makes quite tenuous the assumption that the present radioactivity of a rock at or near the surface of the Earth is the same as that in the past history of the rock (Doe, 1970).

Published dating attempts for quartz by ESR have concentrated on quartz phenocrysts from volcanics and on quartz in fault gouge. Some volcanics might be the rocks most suited to conventional ESR dating, because U apparently can be fixed in the glass phase (Zielinski,1978 and 1981; Zielinski and others,1980), and because these rocks are likely to be more homogeneous on the scale of mms. On the other hand, fault gouges would seem to be highly affected by problems associated with U mobility, because they are usually conduits for water, and redox conditions would determine if U is removed or introduced to be precipated at quartz grain boundaries.

It is important in evaluating conventional ESR dating of quartz to consider that in those published studies (cited above) that have utilized more than one type of ESR center, different values for TD (and therefore different ages) were determined from different centers. The authors of these studies have attributed these discordant results to be due to some secondary effect that has altered the natural signals of some particular center while

not affecting another. There are both theoretical and experimental reasons to suspect that changes in the concentration of a center occurs in response to a change in the electronic equilibrium of the crystal, and that this shift in equilibrium will affect all centers, though to different degrees. It would seem that to have confidence in an ESR age determined by the additive dose method, either that age should be obtained on more than one center, or the response of individual centers to radiation should be shown to be independent of each other.

3. Neutron-calibrated method

Garrison and others (1981) reported on an attempt to date flints of Paleozoic age utilizing what they interpreted to be a peroxy radical ESR signal. They compared the intensities of natural peroxy radical signals in flint with those of samples irradiated in a calibrated fast neutron flux. From this comparison and an approximate knowledge of the total energy deposited in the samples by the neutrons, they were able to estimate the total energy required to produce the natural signals by alpha decay. With a determination of the U and Th concentrations of the flint samples, they calculated the time necessary to produce the natural signals, i.e. the "ages". Most of the ages they reported were within 30% of the stratigraphically determined ages. One of the six calculated ages was an order of magnitude too young.

The method used by Garrison and others, theoretically has an advantage over the conventional method of ESR dating of quartz, in that being based on the rate at which new structural defects

are produced by alpha decay recoil, it need not be limited to quartz less than a few million years old. On the other hand there are a number of assumptions and uncertainties involved in relating the pile produced ESR signals to the natural signals, the flux and spectrum of energies of neutrons in the reactor to the monochromatic nature of *in situ* alpha decays, and two processes with entirely different rates and thermal effects. Finally, there might be some question if the material analyzed is directly comparable to quartz. The reported U concentrations of a ppm and more seem extraordinarily high for low temperature quartz.

IV AN ALTERNATIVE APPROACH TO ESR DATING

1. The Production Of Schottkey-Frenkel Defects

This investigation of the feasibility of dating quartz by ESR is based on the following considerations. Schottkey-Frenkel (SF) defects give rise to two recognizable and measurable ESR centers, an E'center and a peroxy radical (PR) center. SF defects can be produced artificially in quartz by the displacing collisions of fast neutrons with lattice atoms. The suggestion by McMorris (1970) that the PR center is produced naturally in quartz as a result of knock-on displacements by the recoiling nuclei of apha emitting impurities such as U and Th is energetically reasonable and strongly supported by the study of Garrison and others (1983). If one recognizes that the oxygen vacancy and the peroxy linkage constitute a Schottkey-Frenkel pair, it becomes a reasonable inference that E' centers can also be produced by alpha recoil. An oxygen atom displacd by a recoiling nucleus leaves behind an oxygen vacancy and can come to rest in an interstitial position to form a peroxy linkage or a radical. It follows, that for every interstitial oxygen, there is an oxygen vacancy. Neglecting for the moment the possibility of structural annealing of this damage, the abundance of such SF defects in a quartz crystal depends on the abundance of original defects, the number of alpha decays that have occurred, the energies of the decays, and the efficiency of the recoil process to produce SF defects.

The energies of the alpha decays are well known. The efficiency factor depends largely, but not entirely, on the

energies. The number of alpha decays that have taken place depends only on the abundance of the radioactive nuclides, their decay rates, and the age of the quartz.

These fundamental considerations, provide the theoretical basis of a new approach to ESR dating of quartz. If this approach is to be feasible, it must be demonstrated that SF defects do accummulate naturally in quartz over a range of time applicable for dating geologic samples and at a measureable level.

2. Experimental test of feasibility

samples investigated

A suite of quartz bearing rocks whose ages have been determined by more standard methods was selected for this study. The rocks are listed in Table 1. They include granitic plutons, acid volcanics in which the analyzed quartz is a phenocryst phase, and pegmatites. Documentation of the ages listed and rock descriptions can be found in the references cited in Table 1. Samples have been selected that show no petrographic evidence and have no known history of thermal or dynamic metamorphism.

sample preparation

Rocks were crushed in a jaw crusher. The crushed material was sieved to extract that size fraction that mostly closely matched the size of the quartz crystals in the rock and yet contained a significant fraction of single grains. In the case of the volcanic rocks studied here, the quartz used was entirely from the phenocryst phase. Matrix quartz in these volcanics is

largely the product of devitrification and vapor phase crystallization and was removed in the very fine sieve fraction. Quartz was concentrated from the sieved material using high density liquids and an isodynamic magnetic separator. Final purification was achieved by handpicking individual grains under a microscope. Only grains of high optical clarity were selected. Particles of quartz with attached fragments of other minerals or containing inclusions visible at 100X magnification were rejected.

Each quartz sample was etched in cold 48% hydrofluoric acid in an ultrasonic bath. Samples were weighed before and after the etching process to check on weight loss. The weight loss exceeded 7% for each quartz sample. The purpose of this proceedure was to assure that the outermost rims of the original quartz crystals were removed, so that SF defects measured did not include those induced by alpha recoil of radionuclides located at grain boundaries. Microscopic examination of samples also revealed extensive etching along microfractures. Samples were next washed and crushed in high purity water with an agate motar and pestle and then sieved to collect a 70 to 200 micron fraction to be used for ESR analyses. 50 mg size samples were loaded in Vitrosil glass tubes that had previously been analyzed and found to have no detectable ESR signal under the instrumental conditions used for sample analyses.

ESR spectrometry

Analyses were performed with a modified Varian E-12

Spectrometer with microwave operation in the X band. A dual cavity configuration was used so that all signals could be normalized by comparison to the intensity of an external DPPH standard. The reported intensity values of the samples are the relative intensities of the DPPH-normalized signals. All analyses were conducted at room temperature in order to eliminate interference from Al centers. E' center signals were measured at 0.1 mW microwave power and the peroxy signal at 10mW.

In order to test the instrumental reproducibility, a single sample was scanned repeatedly at intervals of three to five weeks. The standard deviation of the mean of 15 measurements of the normalized intensity value was 3% of the mean for both the E'centers and PR centers. Variation of normalized signal intensities between splits of individual samples were less than 3%, except for the very weak E' centers of samples 1 and 2 (Table 1) where variations were were less than 10%.

Intersplit variations include those due to real inhomogeneity as well as artifical variation due to differences in packing density of the quartz grains in the sample tubes. Such differences in packing density results in different spin densities within the analyzing or resonance cavity of the instrument.

results

Figure 2 shows part of the ESR spectrum of sample 10 containing the E' and PR signals. The E'center is best observed at low microwave power (spectrum a), and the PR center, at

FIGURE 2.

Room temperature spectra of sample 11. The signals observed represent the first derivatives of the absorption curves. The "g"factor is the ratio of the magnetic moment to the angular momentum (2.0023 for a free electron) and can be calculated from g=hv/BH. Here B is the Bohr magneton; H, the magnetic field strength at resonance condition; v, the microwave frequency.

(a) 0.10 mW, EPR spectrum of quartz showing prominent E′ center with a baseline crossing at g = 2.001 (crosshair); note weak, broad peroxy signal at slightly lower magnetic field strength H (higher g value).

(b) 10 mW spectrum of the same sample showing strong peroxy signal with turning points at 2.003 and 2.009 (arrows). Though readily saturated at higher power, the E′ center (crosshair at g=2.001) can still be seen.

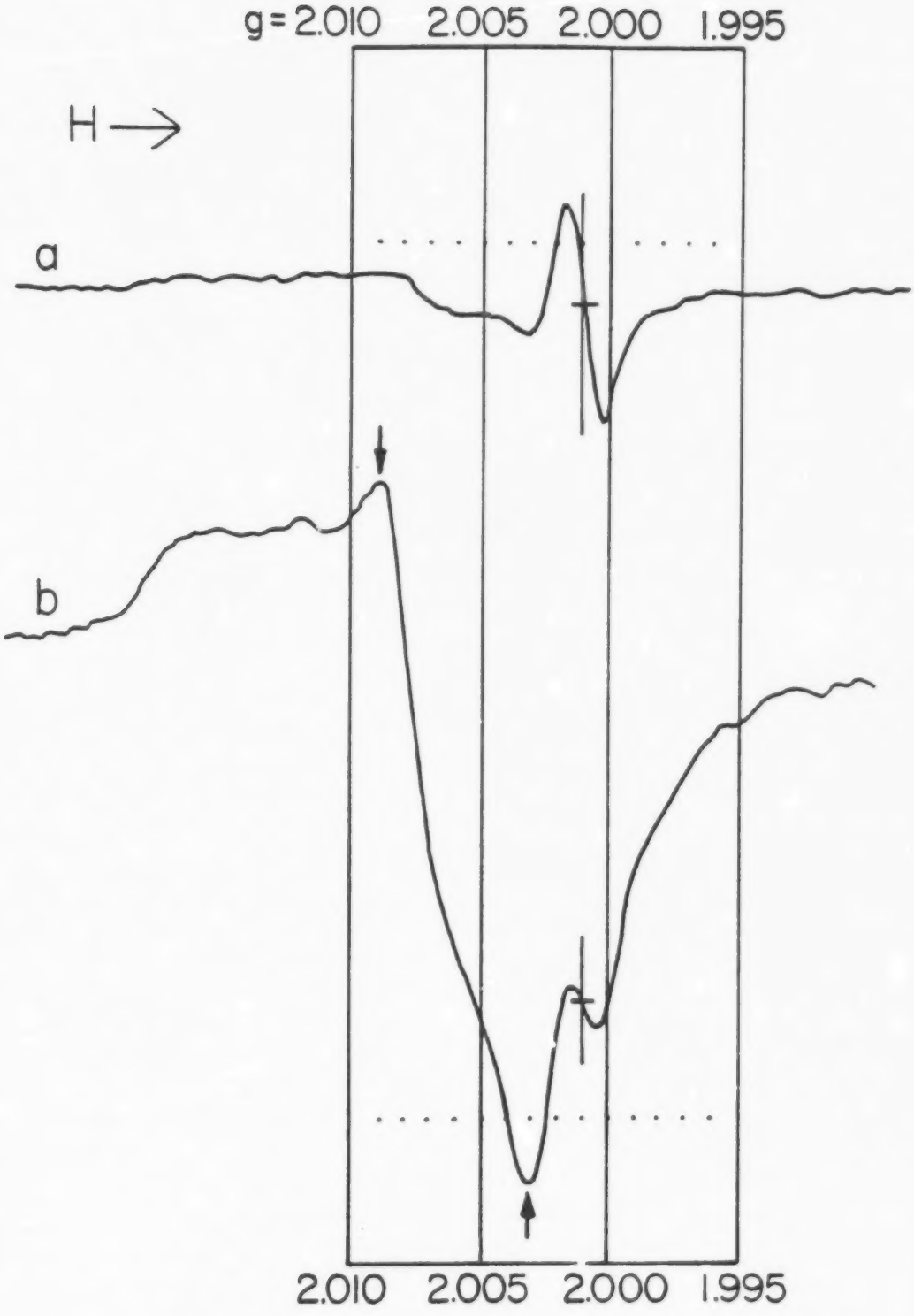


Fig 2

higher power (b). Table 1 gives the relative intensities of natural, room temperature signals of the E′ and PR centers of quartz samples of various geologic ages.

There is a significant positive correlation between the natural ESR signal intensity and age of the quartz (Figures 3 and 4). Linear correlation of signal intensities versus quartz age yield correlation coefficients of 0.83 for the PR center and 0.73 for the E′ center. Adjusted R^2 values are respectively 0.66 and 0.48. F-tests of the regressions indicate a significant correlation (greater than 95% CL) in which up to 66% of the among sample variation in the PR intensities and 48% of the E′ intensities can be attributed to sample ages alone (without considering the variability in alpha activity).

It should be pointed out that the intensity of the natural ESR signals are a good indication of the concentrations of SF defects only when these traps are saturated, or nearly saturated, or to state it in a a more precise way, SF defects are detectable only when they are paramagnetized. The term "saturation" as used here implies a state of electronic equilibrium in which additional ionizing radiation (at room temperature) produces no significant increase in the ESR signal. For most of the samples shown in Figures 3 and 4 this condition is achieved; for two samples it is not.

Gamma irradiation experiments indicate that in samples 7 and 12 the population of oxygen vacancies (traps and structural precursors to E′ centers) is only partially converted to ESR centers, because considerable E′ signal growth is observed with

Table 1. Quartz samples and relative intensities of EPR signals at room temperature and constant instrumental condition (E' center measured at 0.10 mW and Peroxy center (PRC) at 10.0 mW)

Igneous Quartzes	Age (m.y.)	E'Center	PRC	Reference
1. West Moat 9 Rhyolite	.106 (+-) 0.002	1.9	bdl.*	Maniken, E.A. and others (1986)
2. Bishop Tuff	0.727 (+-) 0.150	3.6	bdl.	Maniken, E.A. and others (1986)
3. Turkey Springs	23.4 (+-) n.a.	5.8	cne.**	Chapin, C., (pers. comm.) (1987)
4. Rio Hondo Granite	25.5 (+-) n.a.	5.2	6.1	Lipman, P.W. (1983)
5. Conway Granite	168 (+-) 2	22.9	28.5	Loiselle, M. (1978)
6. Pageland Granite	296 (+-) 5	20.7	28.4	Fullagar, P.D. and Butler, J.R. (1979)
7. Kings Mountain Pegmatite	350 (+-) 10	6.2	43.0	Kish, S.A. (1977)
8. Overflowing Pond Granite	386 (+-) 8	23.6	61.9	Dallmeyer, R.D. and others (1983)
9. Zoura Granite	532 (+-) 7	85.5	96. 9	El-Makhrouf and Feiss (1984)
10. Pikes Peak Granite	1041 (+-) 13	112.3	92.5	Hedge, C.E. (1970)
11. Graniteville Granite	1370 (+-) n.a.	123.6	86.2	Bickford, M.E. (pers. comm.) (1987)
12. Harding Pegmatite	1366 (+-) 186	22.5	75.0	Brookins, D.G. (1979)

* bdl. - below detection limit
** cne. - could not evaluate

FIGURE 3.

Plot of relative intensity (arbitrary units) of peroxy radical center versus age of quartz

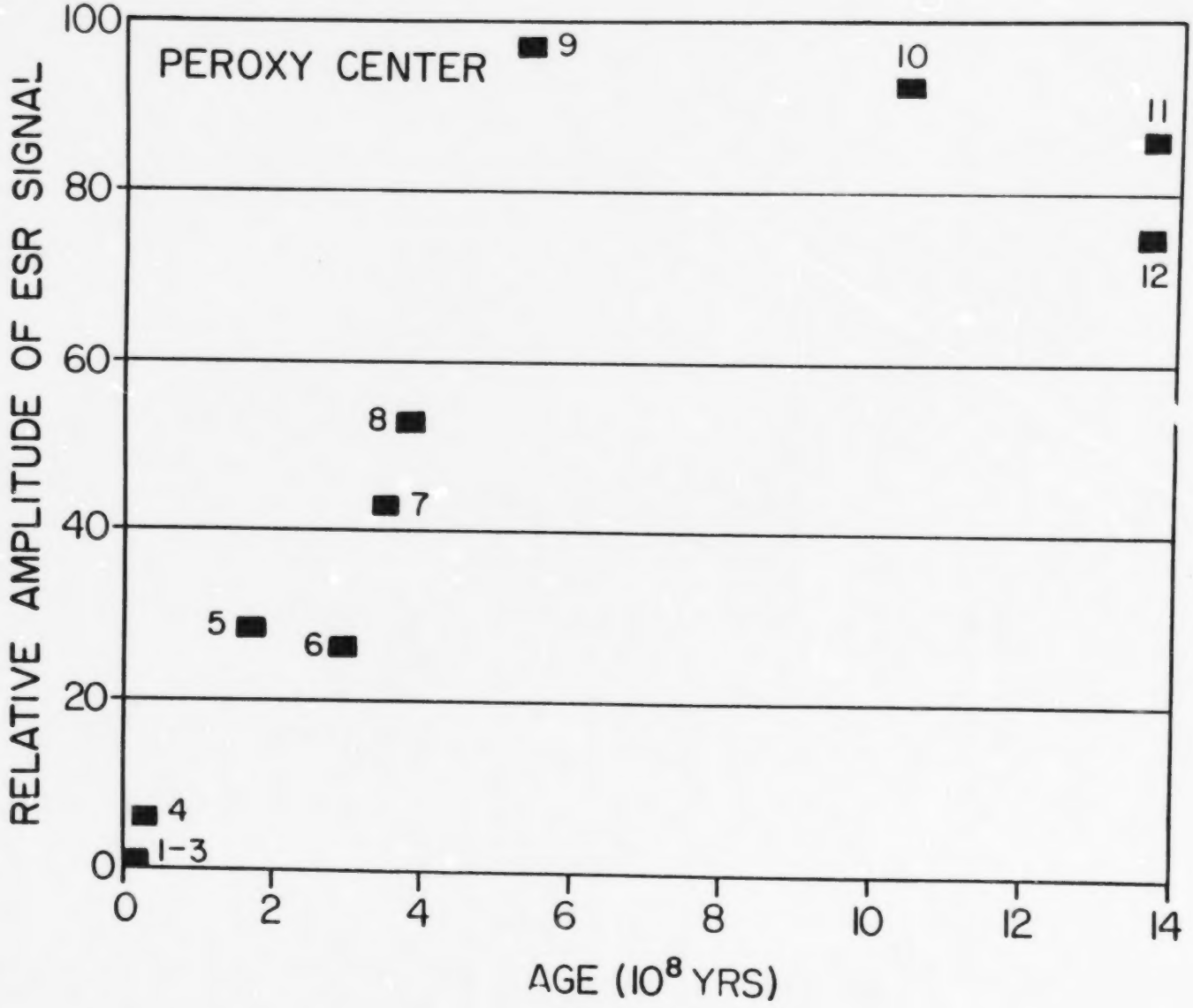

PEROXY CENTER
RELATIVE AMPLITUDE OF ESR SIGNAL
AGE (10^8 YRS)
100
80
60
40
20
0
0
2
4
6
8
10
12
14
9
10
11
12
8
7
5
6
4
1-3

Fig 3

FIGURE 4.
Plot of relative intensity (arbitrary units) of E'center versus age of quartz

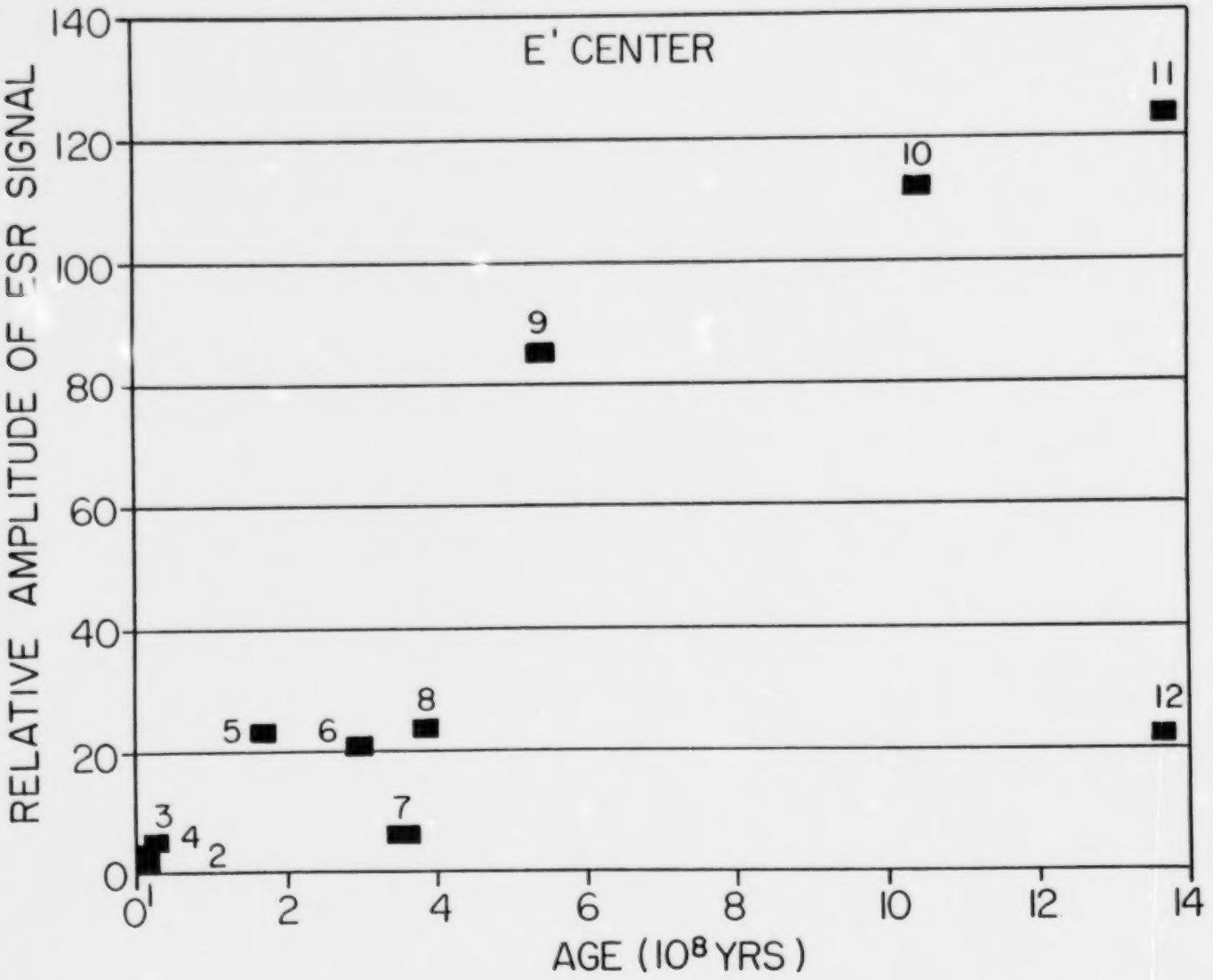

E' CENTER
RELATIVE AMPLITUDE OF ESR SIGNAL
AGE (10^8 YRS)
0
20
40
60
80
100
120
140
0
2
4
6
8
10
12
14
1
2
3
4
5
6
7
8
9
10
11
12

Fig 1

artificial gamma radiation. Results of these experiments are given in Appendix A. It is difficult to actually measure the increase of the E' center under the standard conditions adopted for this study, because a large interfering Ge signal appears in these samples, when they are irradiated. However, it appears that the staurated E'center for sample 12 might be as much as six times larger than the value given in Table 1 and plotted in Figure 4. This estimate is made from the relative intensities of the low-field, half-signals of the natural and gamma saturated E'centers (spectra 'a' and 'e', Fig.1, Appendix A). It can be seen from Fig.4, that sample 12 greatly reduces the correlation of age vs intensity for the E'centers. If the saturated E'center (roughly 6x greater than the natural value) were plotted instead of the natural signal, the correlation coefficient would be significantly higher. Thus the correlation of oxygen vacancies with age is significantly stronger than that indicated by the E'center measurements.

Neither the E' or PR center signals of the other samples that are over 1 m.y. old and have been tested are increased by purely ionizing gamma irradiation. Presumably the traps associated with these samples are naturally saturated (or nearly so) in these samples. However bombardment with fast neutrons does increase the concentration of E'and PR centers (see for example Figs. 5 and 6). Thus it appears that knock-on displacements in the lattice are producing additional SF defects.

FIGURE 5.
a) natural E'center that could not be increased above its natural intensity with gamma radiation, b) the sample after being irradiated with fast neutrons. Both spectra obtained at 0.10 mW microwave power.

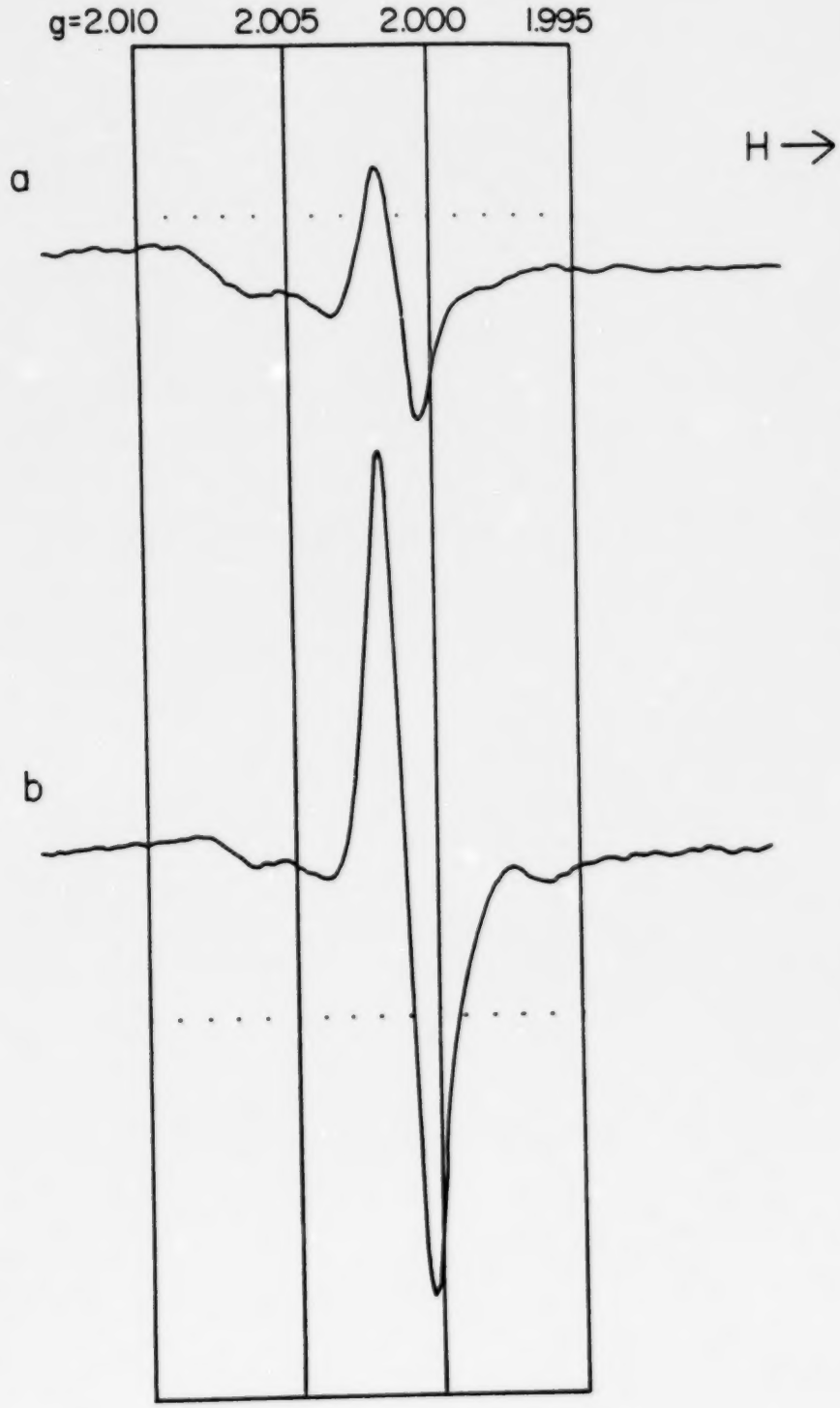


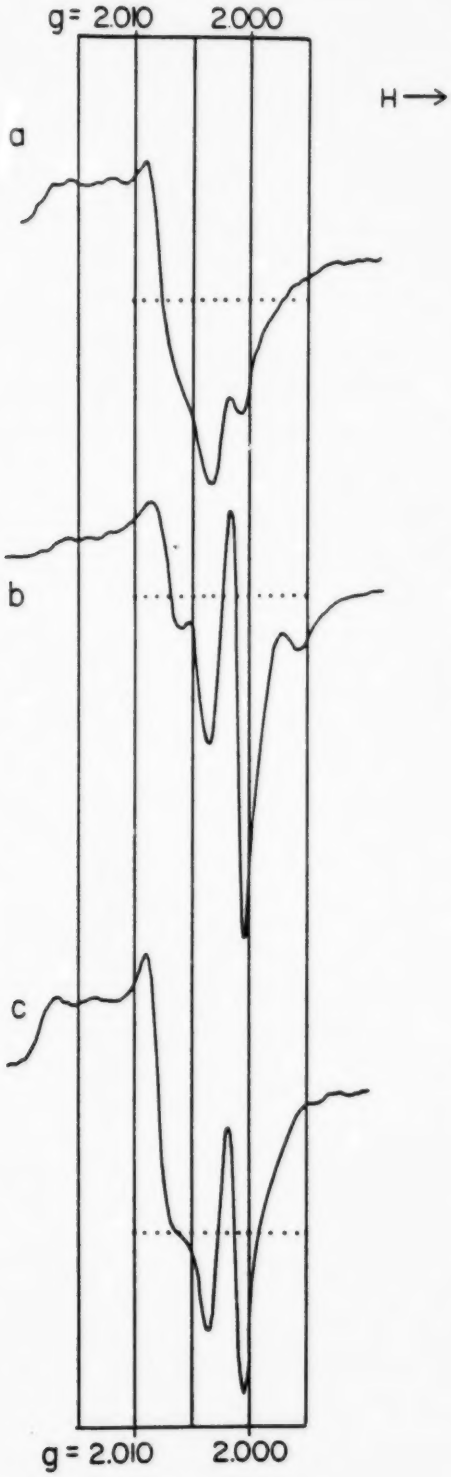
Fig 5

FIGURE 6.

a) natural peroxy center which could not be increased by gamma radiation (note weak signal that appears as a small shoulder on the peroxy at 2.005).

b) the same sample after fast neutron irradiation; The intensity of the peroxy signal actually appears to have decreased due to growth of interfering signal and large growth of E'center.

c) That the lattice defects giving rise to peroxy centers were actually increased is seen after brief (15 minute) heating at 325 C. The superimposed signal is reduced nearly to its natural state, while the peroxy signal is larger than in its natural state.


g= 2.010
2.000
H⟶
a
b
c
g = 2.010
2.000

3. Discussion of the dating method

Results of this study supports the conclusions of McMorris (1970) and Garrison et al. (1981). The PR center in natural quartz increases with time. Additionaly the present study indicates that oxygen vacancies also accumulate naturally over geologic time. Experimentally, the SF defects can be produced by fast neutron bombardment. The only mechanism likely capable of naturally producing Schottky-Frenkel defects in quartz and duplicating the effect of fast neutrons are the elastic collisions of recoiling, alpha-emitting nuclides with Si and O atoms. For example the recoiling nucleus from the alpha decay of a ^{238}U atom dissipates approximately 70 Kev of energy in the quartz lattice. This energy far surpasses the Si-O bond energies; lattice displacements are produced by primary knock-ons and cascades. That single recoil will result in more than 1000 displacements being produced (displacements calculated using the TRIM 88 program; Ziegler and others, 1985). The displaced oxygens that leave behind oxygen vacancies can become interstitial oxygens that form the peroxy linkages.

Thus the rate at which SF defects are produced in quartz is a function of the concentration of nuclides that undergo alpha decay and the efficiency of recoil processes to produce the defects. This relationship can be expressed by the following equation which gives the total number of defects produced by all of the alpha active nuclides (i) in a single decay chain.

$$D = \sum_i C_i f_i (e^{\lambda t_i} - 1) + D_o \qquad (1)$$

D = concentration of S or F defects (#/gm of quartz)
D_o = original conc. defects at time zero
C_i = conc. of nuclide i (atoms/gm quartz)
f = efficiency factor (number of defects produced/ decay)
λ_i = decay constant for nuclide i
t = age of the quartz

Some SF defects must be original. The equilibrium value for SF defects forming during crystal growth is directly proportional to temperature of crystallization (Kittel, 1971). Thus the highest concentration of original SF defects should be those in volcanic phenocrysts that were quenched at their high temperature equilibrium value. Current indications of preliminary measurements of volcanic phenocrysts less than 10^6 years old suggest that original defects might be only a minor fraction of SF populations in quartzes older than several million years (obviously this will depend on the alpha activity of the quartz). Such indications are a) the trends indicated by the data in Table 1 and Figures 3 and 4 seem to originate at a zero value of intensity and age, b) the low values of the data set are for volcanic phenocrysts, and c) attempts at room temperature analyses of 500 and 10,000 year-old volcanic phenocrysts resulted in undetectable E' and PR signals. Considerably more analyses are needed to adequately assess this situation, and these are in progress.

V SUMMARY OF CONCLUSIONS

1. As a result of ambient, ionizing radiation in rocks, two ESR centers develop from Schottky-Frenkel defects in quartz.

2. SF defects are produced by the displacement of O and Si atoms in the crystal lattice as a result of elastic collisions initiated by the recoil of alpha-emitting nuclides present as impurities. The natural accumulation of these SF defects in quartz is a time dependent process.

3. The rate at which SF defects become ESR centers (rate of paramagnetization or trap filling) is, in most rock environments, faster than the rate at which the defects are formed. In these cases, the ESR centers are a measure of the defects themselves. In cases where this might not be true, gamma radiation can be used to saturate the traps, so that they can be measured.

4. Though the E′ center in particular has been reported to have such a short mean life that it can not be used for dating beyond a couple of million years (Ikeya et al., 1982), its structural precursor (the oxygen vacancy) is far more stable and increases in number with time. The rate at which E′ centers develop from oxygen vacancies in most cases exceeds the rate of decay of the centers. In cases where this is not so, (such as with samples 7 and 12), artificial gamma radiation can restore those decayed centers.

5. Judging from the samples reported here and a few other low temperature measurements of volcanic quartz phenocrysts, it appears that the concentration of radiation induced SF defects in

quartz samples older than ten million years far exceeds the concentration of original defects. Obviously this will depend on the alpha activity of the quartz, and further study is needed.

6. The advances made by other investigators (cited earlier) indicate that, under favorable conditions, it is possible to date quartz younger than a few million years old by ESR methods. The results of this study indicate that utilizing a different approach to ESR dating, one based on the natural accumulation of alpha-recoil produced Schottky-Frenkel defects, the development of a long ranging quartz geochronometer is feasible.

VI PROBLEMS REMAINING AND RECOMMENDATIONS

Practical application of this quartz geochronometer will require 1) measurement of the relative abundance of SF defects, 2) determination of the alpha activity, 3) evaluation of the efficiency factors, and 4) an understanding of the thermal stabilities of the SF defects. At present these seem to be achievable tasks, and they are under active investigation.

1. Measurment of the relative abundance of SF defects

This can be done now, but there is room for improvement in accuracy, sensitivity, and precision. The defects can be measured only when they are paramagnetized as an ESR center (occupied by an unpaired electron). The observation that the ESR centers in most quartz samples older than a few million years old are saturated indicates that in most cases, the natural rate of trap filling is greater than the rate of defect formation. This can be tested in individual cases, and artificial gamma irradiation can assure saturation. Since measurements of the ESR centers are made relative to a artificial standard (DPPH), and could additionally be made to a natural quartz standard of known age, it might be a better method to routinely subject all samples and quartz standard to artifical gamma irradiation until saturation is attained.

Sensitivity can be significantly increased by utilizing Q band microwaves and performing analyses at lower temperatures. Significant improvement in measuring signals can be made by digitizing data, performing double integration to obtain

absorption curves, and subtracting interfering signals. A computer library of signal shapes at various intensities will be useful in corrections for interference.

2. Determination of the alpha activity

Though quartz is commonly regarded as a pure compound, a number of elements can substitute for Si. Still more can be included in the large (3 angstrom) channels that spiral around the c-axes. U and Th are included in quartz only in very low concentrations. The careful microscopic examination required to achieve high purity, inclusion-free samples makes large sample sizes impractical for routine analyses. The combination of small sample size and low concentration makes it very difficult to determine the activity of U and Th by standard counting methods.

An isotope dilution method utilizing thermal ionization mass spectrometry has been employed in this study to determine the U and Th concentrations. A brief description of the method and preliminary results are given in Appendix B. It is expected that it will be sufficient to measure the U and Th concentrations and calculate the activity of their radioactive daughters, though a check for radioactive equilibrium should be made.

3. Evaluation of the efficiency factor

The efficiency factor, 'f' in equation 1 above is a measure of the overall efficiency of the recoil process to produce SF defects in quartz. Since the energies of the alpha decays and the Si-O bond strength are well known, it is possible to make a reasonable estimate of the number of displacements that will be

produced by a given concentration of U and Th. This was done by McMorris (1970) utilizing the method outlined by Seitz (1949). A computer simulation of defect formation based on a program developed at IBM by Ziegler and others (1985) is currently being tested to calculate the efficiency of alpha-recoils to produce SF defects.

Probably the best way of determining the efficiency factors is by experimentation. In collaboration with Bob Laudice of AT&T Bell Labs, an experiment has begun to determine the efficiency directly. This will involve monitoring the build up of E′ and PR centers over a period of 12 months or more in an artificially grown quartz crystal that has been doped with a known amount of a short-lived alpha emitting radionuclide. This should permit a direct determination of the growth of ESR intensity associated with SF defect (gamma radiation will be done to test or assure saturation).

4. Thermal stabilities of SF defects

There is very little information available regarding the stability of SF defects in quartz. The few investigations that have been made on the stability of the ESR centers do not bear directly on the dating method based on accumulation of SF defects, for even after fading or thermal annealing, the E′ and PR centers can be regenerated artificially to permit detection of the SF defects, as long as these structural defects remain.

There can be no doubt that the SF defects are far more stable than the ESR centers. The activation energy required to

rearrange atoms in the quartz lattice is much greater than that necessary for the electron transitions. Furthermore that experiments have shown that thermally annealed E' and PR ESR signals can be regenerated with gamma irradiation is evidence that the structural defects survived the annealing. Finally the data presented in this report indicate that the SF defects are stable enough to accumulate at modest geologic temperatures, over hundreds of million years.

Precise knowledge of the stabilities of SF defects can be acquired by experimental thermal annealing at different temperatures for different lengths of time. Extrapolation of of laboratory annealing conditions to annealing temperatures on a geologic time scale is permitted by the Arrhenius relation

$$t = f \times \exp(E/kt).$$

in which f is a constant, T the annealing absolute temperature, t the duration of the heating at temperatur T, E the activation energy, and k the Boltzmann constant. In terms of the natural logs, the expression has the form of the linear equation

$$\ln t = E/k \times 1/T + 1/f.$$

The activation energy can be evaluated from the slope of a line defined by a plot of ln t vs 1/T determined from the laboratory measurments. Extrapolation of the line will provide the information on the thermal annealing temperatures on a geologic time scale. This is the same technique that has been successfully applied in fission track dating.

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APPENDIX A

(segment of an unpublished manuscript by W.J.Rink and A.L.Odom)

Shimokawa and others[1] first used electron spin resonance (ESR) Ge signals to date quartz from a welded tuff. Shimokawa and Imai[2] compared the ESR ages of the Ge, OHC, and Al center with fission track and thermoluminescence ages to evaluate the ESR age thermal altered welded tuffs. We have observed the Ge, E′, and oxygen hole-related[3] (an analog of the OHC in fused silica[3,4]) signals in three pegmatite quartzes. In all three quartzes, a fading component of the room temperature Ge signal was present. With artificial gamma irradiation, a robust E′ signal growth occurred subsequent to an initial stage of growth of only the Ge signal.

The Harding pegmatite (1366 m.a old[5]), the Kings Mountain pegmatite (350 m.a.[6]), and another pegmatite of probable Devonian age are all quartz and spondumene-bearing (Li-rich) assemblages. The quartz samples were all prepared as follows: HNO_3 cleaning, cold 48% HF etching, distilled water rinsing, 90-100°C air drying, agate mortar and pestle hand crushing, sieving to 70-210 micron particle size, andf weighing of 50 mg samples. An X band spectrometer was (Varian E-12) was operated at room temperature. Artificial gamma irradiations were performed using a calibrated ^{137}Cs source. An external DPPH standard was monitored using a TE-104 dual cavity configuration to normalize instrument responses.

Figure A1 shows the change of the Harding quartz sample with

gamma irradiation as observed at 0.10 mW microwave power. The Harding response is typical of all three samples. The native signal (Fig. Ala) shows only the E′ center (formed by a hole being trapped at a doubly electron-occupied oxygen vacancy[7]) signal. Figure 1a shows the immediate appearanc of the Ge center signal upon irradiation which is due to trapped electrons at substitutional Ge sites[8]. Subsequent strong growth of the Ge center signal made it difficult to adequately assess the actual intensity changes of the Ge and E′ signals, because they overlap one another. However Fig. Ale shows clearly the onset of a robust growth of the E′ center that was strong enough to overcome the encumbering Ge center. In all three quartz samples, both signals continue to increase until a sufficient exposure caused both to stop increasing nearly simultaneously.

The Ge signal had a fading component at room temperature. This is probably the $[GeO_4]^-$ species[8]. The $[GeO_4/M^+]^o$ center^o is the stable component with primarily $M^+ = Li^+$. The fading component was monitored in two of the quartz samples after 50 kilorads dose in each. Room temperature half-lives of 32 and 38 minutes were observed in the Harding and Kings Mountain quartzes respectfully. The initial ratio of fading/stable component was also slightly different, 0.3 and 0.25 respectfully. As the saturation level of cnters was approached, no unstable component was observed. This suggest that the fading is probably conversion of $[GeO_4]^-$ to $[GeO_4/M^+]^o$ by Li^+ and Na^+ diffusion along the c-axis channels.

When the Ge signal is used to calculate ESR ages via the

additive dose method, care must be taken to assure that only the stable component is used, because the two component signal would yield inaccurate equivalent doses.

Figure A2 shows the irradiation induced changes in the oxygen hole related center (with powder pattern turning points at g = 2.0035 and 2.0100) as observed at 10 mW power. This center appears to experience a decrease in intensity, although interference from the Ge signal makes it difficult to quantify the changes. The E'cnter is absent from the spectra due to power saturation effects. The precursor of OHC in fused silica is an interstitial oxygen[4]. The oxygen hole related center in quartz may be induced by fast neutron irradiation[9] and therefore is likely associated with displaced oxygens. Such displacements occur naturally in quartz by alpha recoil of uranogenic and thorogenic nuclides[10].

There are at least three sites in quartz which are potential hole traps: substitutional Al[8], oxygen vacancies, and interstitail oxygens (peroxy linkages[3]). Upon hole-trapping, these sites become potential electron acceptors that occupy energy levels just above the valance band. Substitutional Ge is a potential electron trap. After trapping an electron, it becomes a potential donor of an electron occupying an energy level slightly below the conduction band. Exchange reactions among radiation induced paramagnetic electron and hole centers are reflected by changes in their ESR signals.

FIGURE A1

Irradiation induced changes in the 0.10 mW powder pattern ESR spectrum of the Harding pegmatite quarz. H is magnetic field. cross shows approximate cnter of E'center signal. Circled cross gives approximate center of Ge signal.

a) native signal before irradiation (gain x1)
b) after 5 kilorads dose (gain x1)
c) after 20 kilorads (gain x1)
d) 70 kilorads (gain x0.5)
e) 150 kilorads (gain x 0.25)

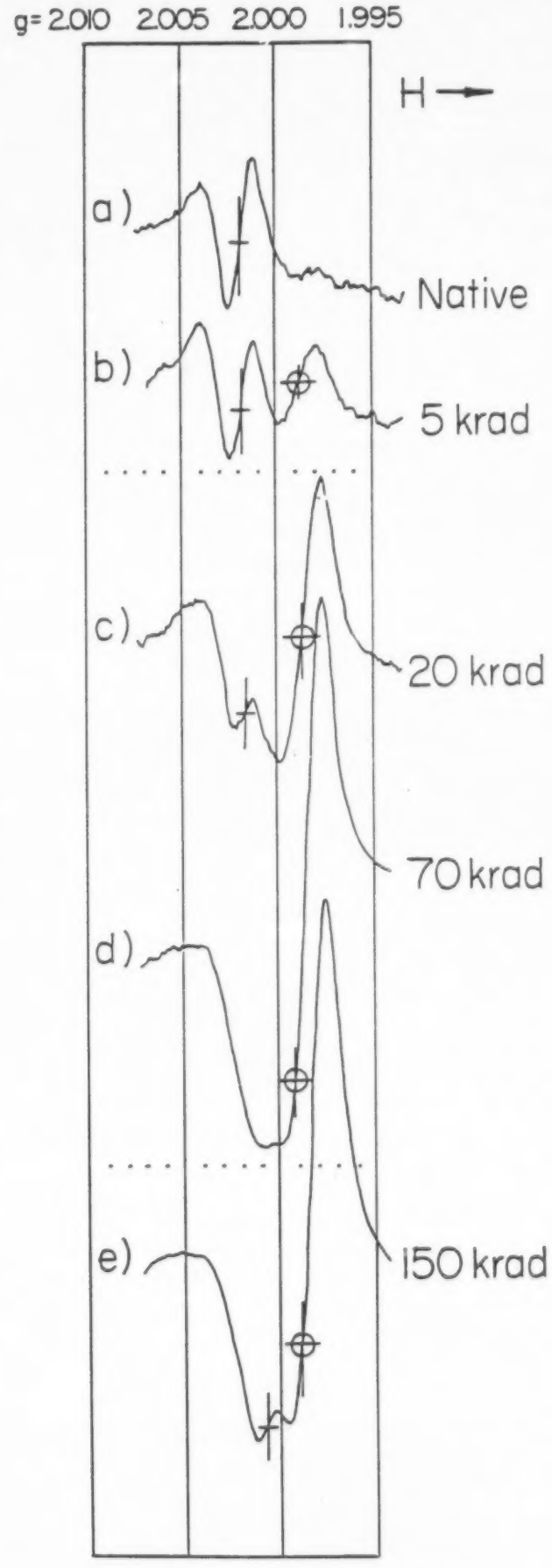
g= 2.010 2.005 2.000 1.995
H
a)
Native
b)
5 krad
c)
20 krad
70 krad
d)
e)
150 krad

Fig A1

FIGURE A2

Irradiation induced changes in the 10.0 mW powder pattern of the Harding pegmatite quartz. H is magnetic field strength. Circled crosses show approximate center of Ge signal; arrows indicate turning points of the oxygen hole related signal.

a) native signal before irradiation (gain x1)
b) after 5 kilorads dose (gain x1)
c) 20 kilorads dose (gain x0.5)
d) 70 kilorads dose (gain x0.1)
e) 150 kilorads dose (gainx).1)

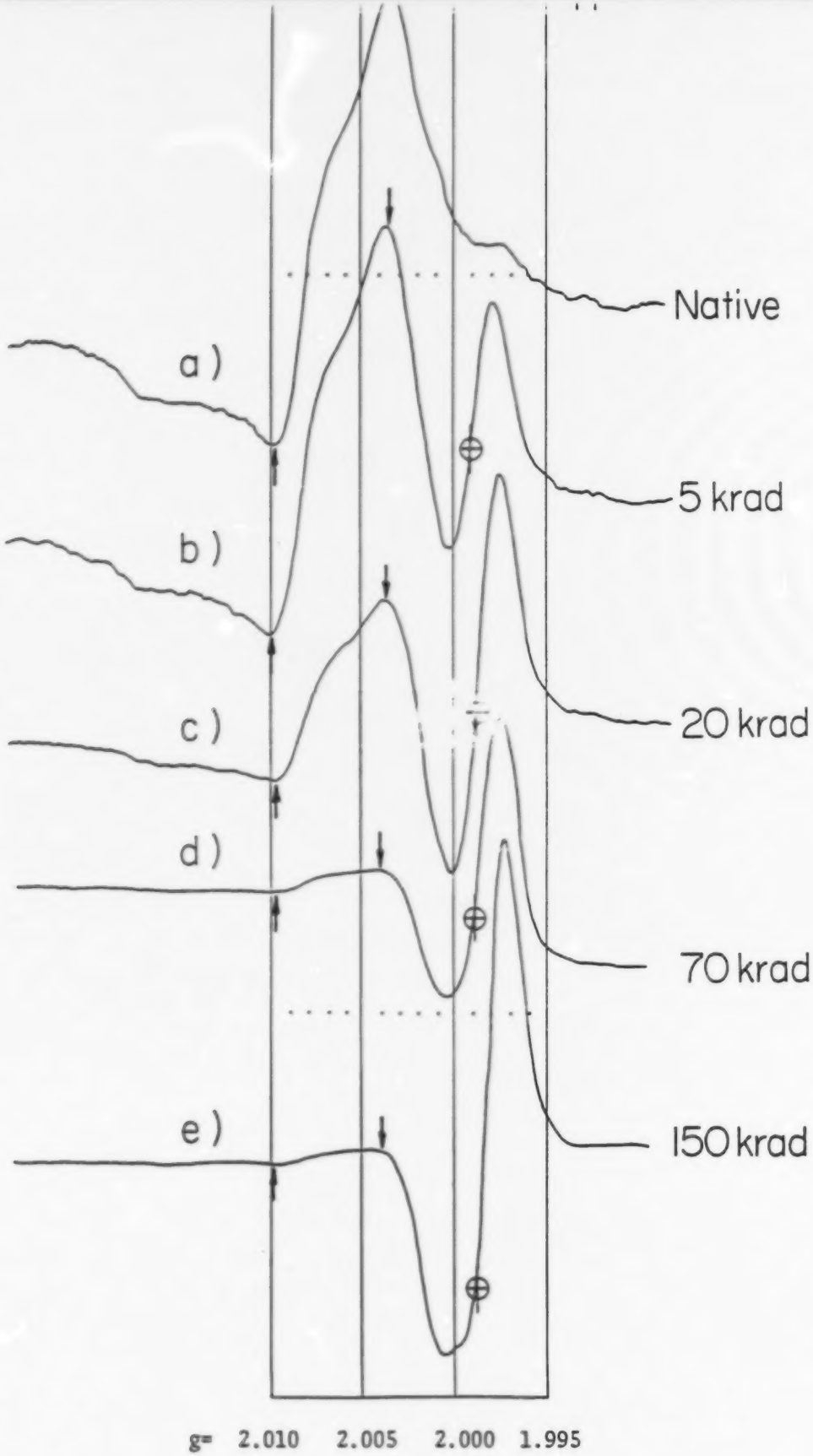
Native
a)
5 krad
b)
20 krad
c)
d)
70 krad
e)
150 krad
g= 2.010 2.005 2.000 1.995

Fig A2

Appendix B

A preliminary study has been made to determine if the quartz samples used in this study contain U and Th at levels that can be accurately measured. A standard isotope dilution method was used for the U analyses, in which a known amount of ^{235}U was added to a solution of the quartz sample, the $^{238}U/^{235}U$ ratio of the mixture measured by thermal ionization mass spectrometry, and the ^{238}U concentration of the sample calculated. For Th analyses, a ^{230}Th isotopic tracer was added, and and the $^{232}Th/^{230}Th$ ratio measured.

We can presently measure with adequate precision as little as 10^{12} atoms of U. Measurements of U in a few quartz samples reveal concentrations in the range of part per billion range to 100 ppb. Initially sample sizes approaching 1 gram of quartz were used. Preparation of samples so large is extremely inconvenient, since grain-by-grain microscopic examination of the finely crushed quartz is necessary to avoid other mineral grains and inclusions in the quartz.

The ionization efficiency for Th in the mass spectrometer source is far less than that for U. As yet we can not accurately measure the concentration of Th. Apparently in the few samples of igneous quartz analyzed, Th is less abundant than U. Installation of a new resonance ionization source mass spectrometer at Lamont Doherty Geological Observatory will certainly provide the enhanced sensitivity to work with smaller samples and provide the capability for the Th analyses. Construction, installation, and testing of this system is behind

schedule. It is anticipated to be on line in November, 1988.

Figure B1 is a plot of the relative intensity of the natural peroxy radical signal of four quartz samples versus the product of their age (in years) and their uranium concentrations (in grams/100 mg of quartz). The sample numbers refer to those samples in Table 1. These same samples are included in the plot of natural signal intensity versus age (Fig. 3). When the ages are normalized to the uranium concentration, the data form a significantly more linear array. This is presented as additional evidence that the concentration of the defects reflected in the EPR intensity is a function of age and alpha activity of the quartz samples, though it is realized that 4 samples constitute a very small population, and radiation damage from Th series radionuclides must be considered.

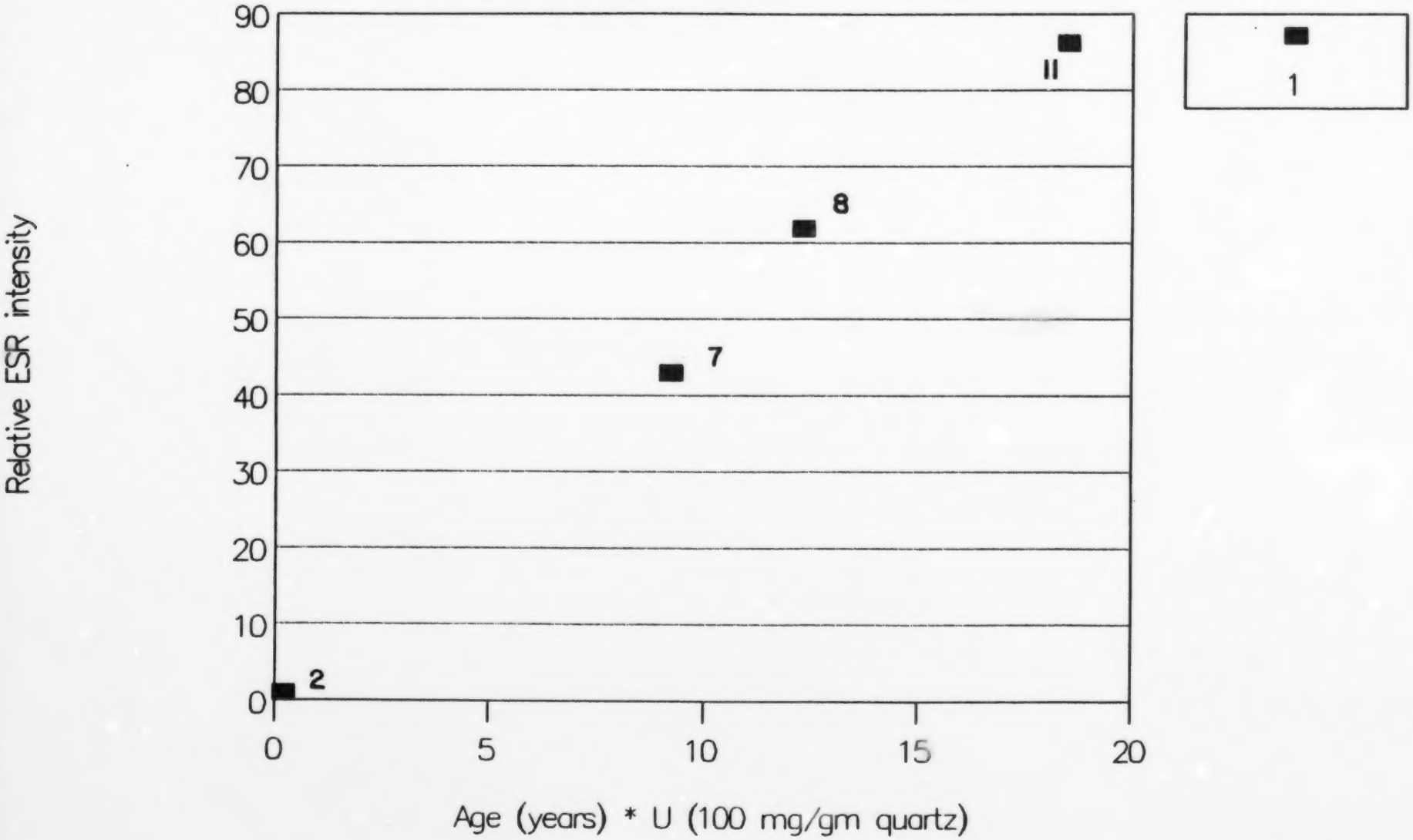
Relative ESR intensity
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
11
8
7
2
1
Age (years) * U (100 mg/gm quartz)

Fig is 1